

Modification of Electrode Surfaces Via Chromium Deposition

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INTRODUCTION

Electrodes are analytical tools used to monitor electron movement in chemical reactions. Typical electrodes have a large surface area and exhibit linear diffusion of chemical species, producing background noise in readings. Microelectrode arrays reduce this noise by exhibiting radial diffusion and thus are highly valuable to electrochemistry research.

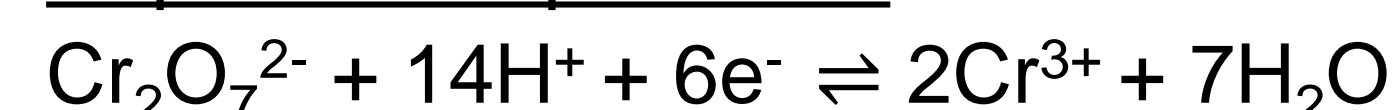
Microelectrode arrays are costly to produce and cannot be repaired if broken. This project explores the efficacy of producing microelectrode arrays that are cheap, easy to construct, and renewable. Such an array allows for greater electrochemical study at undergraduate universities while also providing insight into the oxidation and reduction processes of chromium.

METHODS

DEPOSITION EXPERIMENTS

- 1 mM $K_2Cr_2O_7$ in 0.1 M KCl

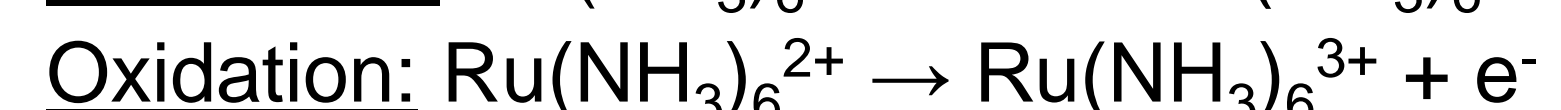
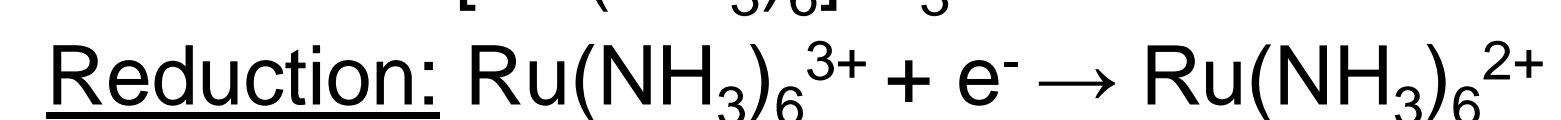
Deposition Equilibrium:



The forward reaction is favored at -1000 mV. The Cr^{3+} that is formed attaches to the electrode surface, inhibiting further electron transfer at that site. Deposition was performed by Direct Current Potential Amperometry (DCPA) where the electrochemical cell was held at a potential of -1000 mV for varying lengths of time.

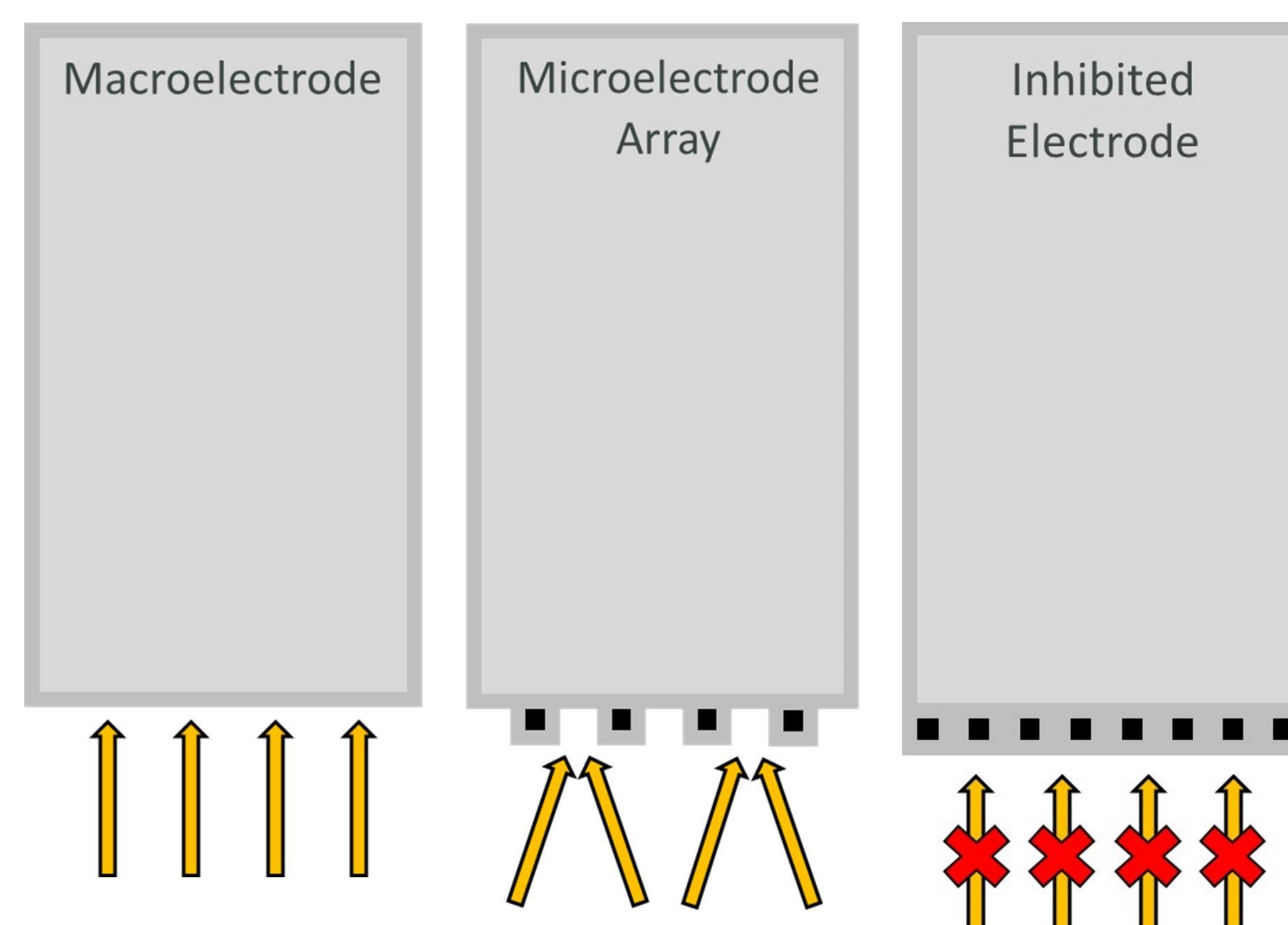
MODEL SYSTEM MONITORING

- 1 mM Hexaammine-ruthenium(III) chloride $[Ru(NH_3)_6]Cl_3$ in 0.1 M KCl



We use ruthenium hexamine (RuHex) as a model system to test the Cr coverage of the electrode. Reduction and oxidation of ruthenium hexamine can be observed between 250 mV and -500 mV. Two experiments were performed for monitoring: Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV).

A Glassy Carbon (GC) electrode and 0.1 M KCl background electrolyte was used for all experiments.

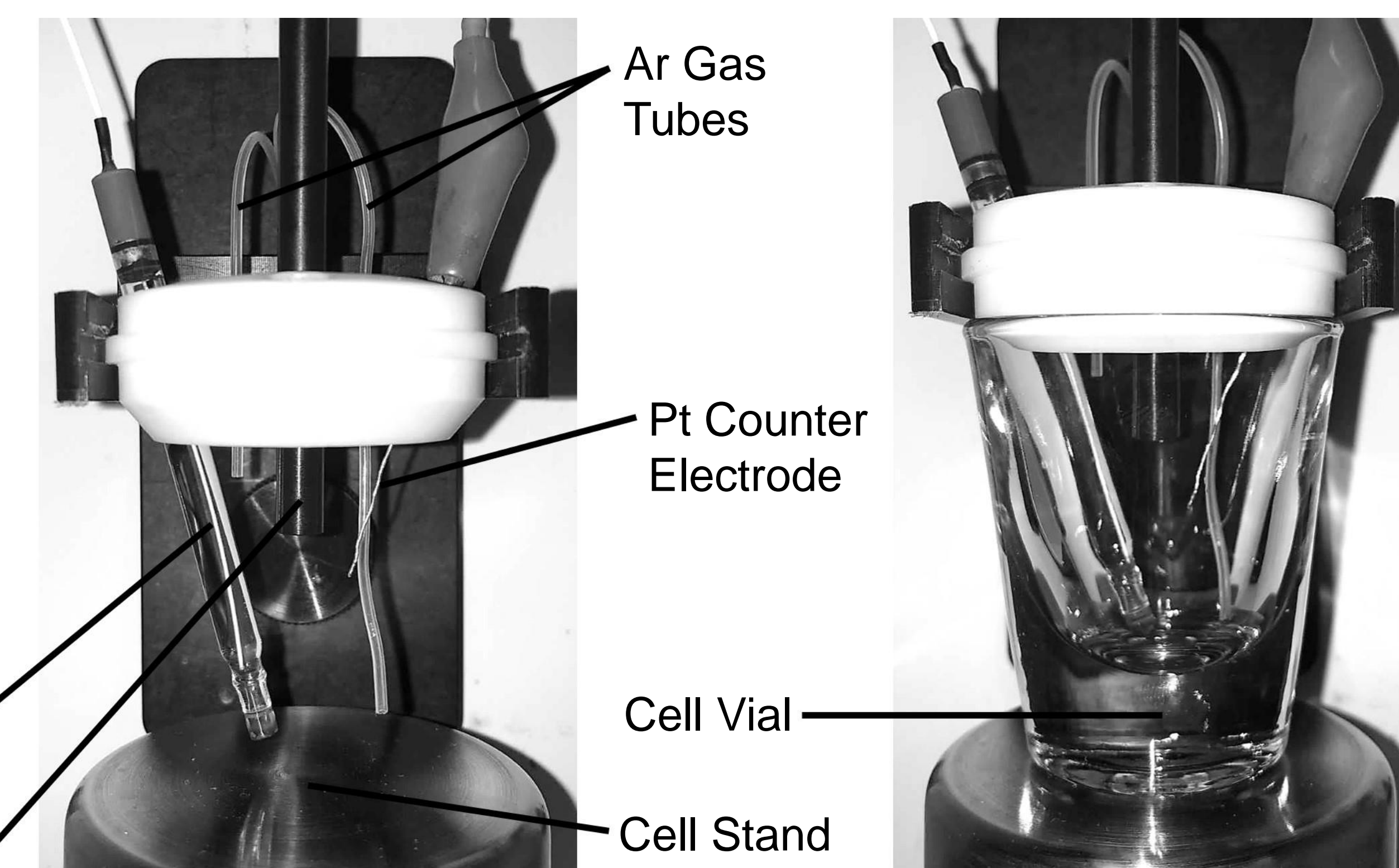


RESULTS

← Figures 1-3. Schematic of microelectrode production via deposition of Cr. Black boxes signify inactive sites where Cr has been deposited.

→ Figures 4-5. Labeled images of the cell used for all experiments. Figure 4 is without the cell vial, Figure 5 includes the vial. Vial contained KCl for background, $K_2Cr_2O_7$ for Cr deposition, or RuHex for system monitoring.

Ag/AgCl Reference Electrode
Glassy Carbon Working Electrode



CVs of RuHex with Varying Time Intervals of Cr Deposition

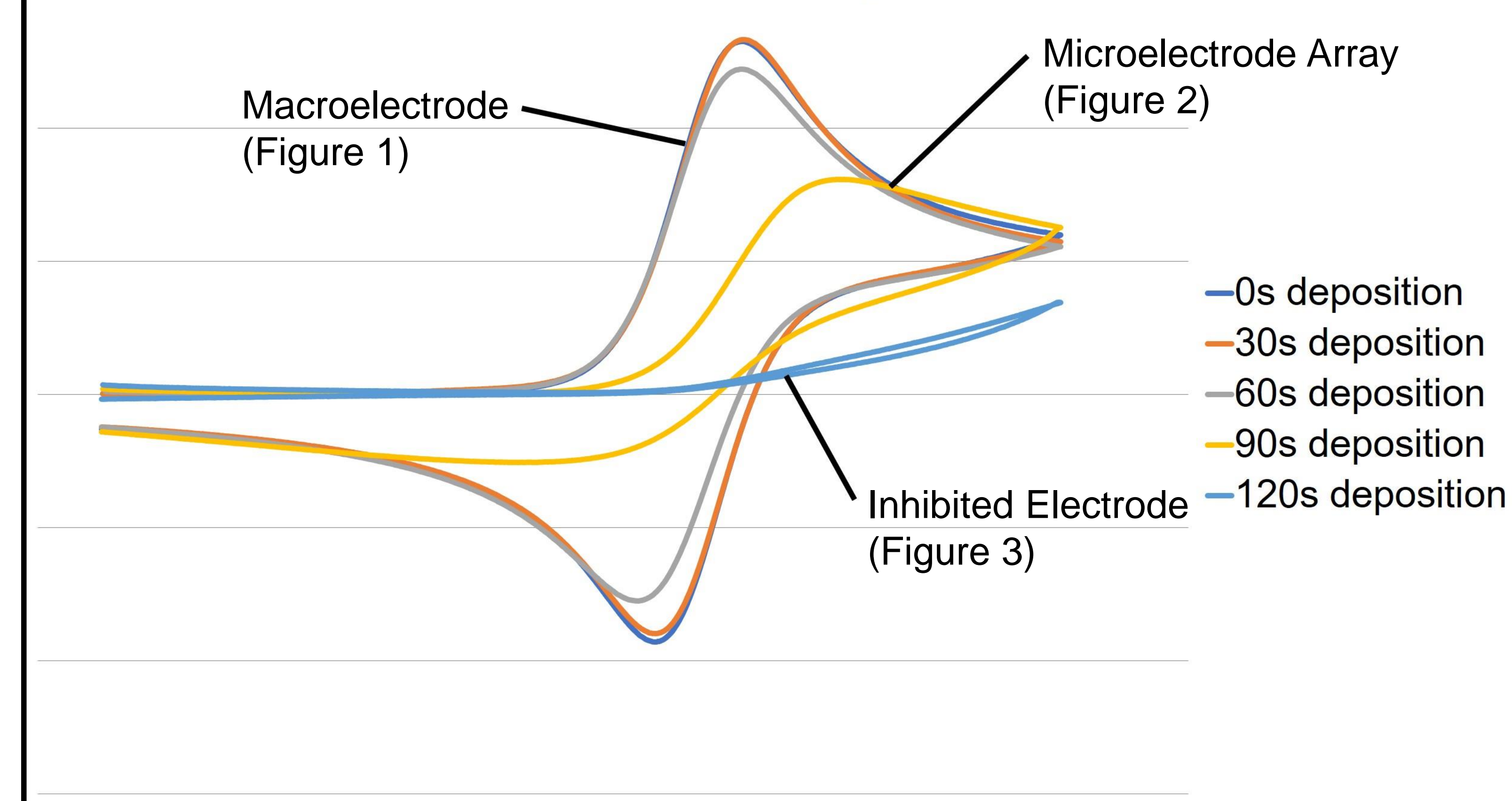


Figure 6. CVs produced in RuHex with a GC electrode after varying intervals of Cr deposition. As the electrode spends more time at -1000 mV during deposition, the reduction and oxidation of RuHex decreases. The CV experiments were performed from 250 mV (left-most x-value) to -500 mV (right-most x-value) back to 250 mV.

DPVs of RuHex with Varying Time Intervals of Cr Deposition

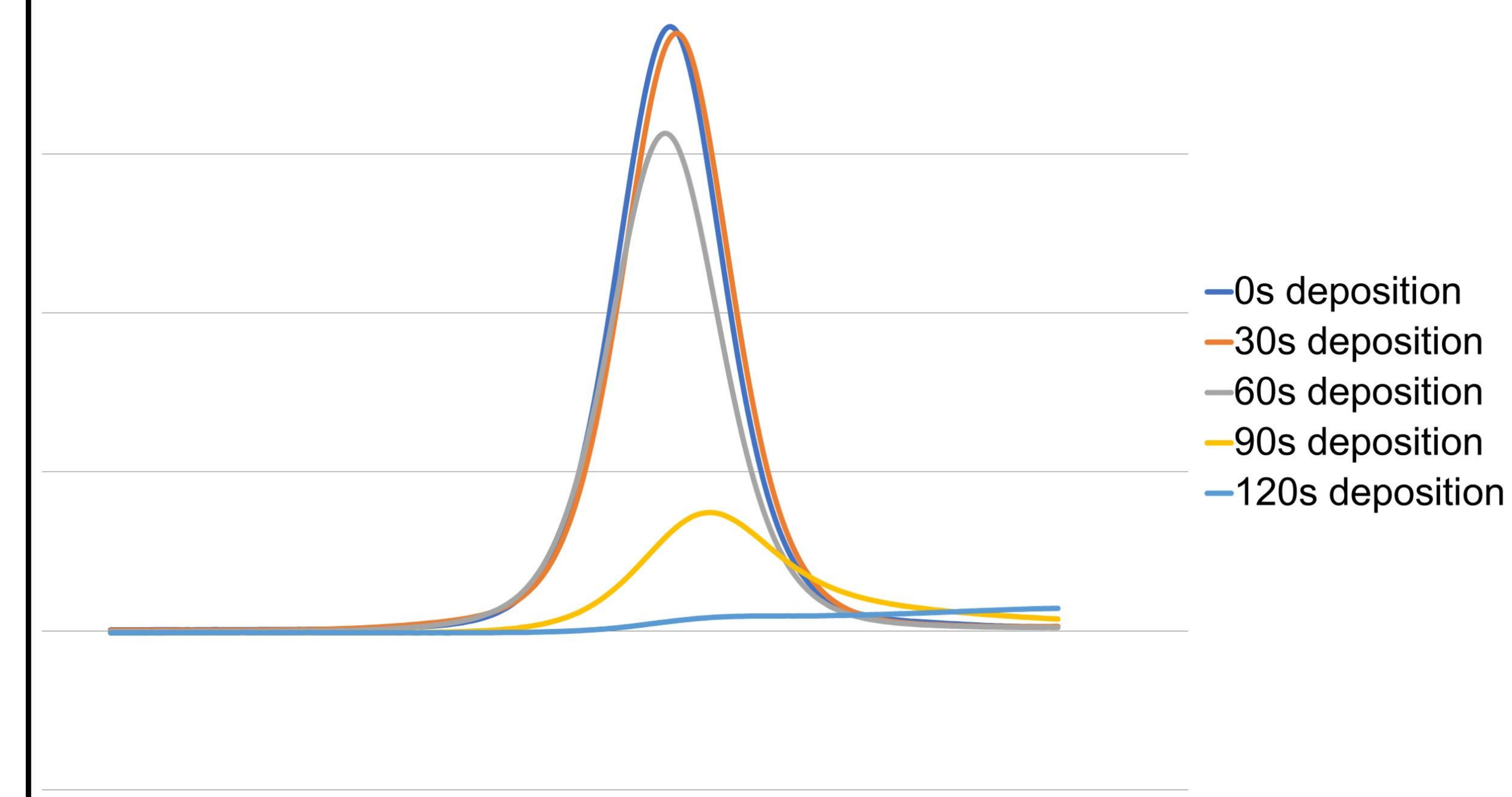


Figure 7. DPVs produced in RuHex with a GC electrode after varying intervals of Cr deposition. As the electrode spends more time at -1000mV during deposition, the reduction of RuHex decreases. The DPV experiments were performed from 250 mV (left-most x-value) to -500 mV (right-most x-value).

CONCLUSIONS

Deposition of Cr onto the electrode surface varied with time at a low concentration of $K_2Cr_2O_7$. This process provides a cheap and easy method for producing microelectrode array behavior. Results, however, were not consistent with time intervals, making them difficult to produce.

FUTURE DIRECTIONS

The methodology must be refined to produce more reproducible results. One option is to use an alternative method of deposition. Results will also continue to be compared to the Kondo et al. publication that describes their method of microelectrode array production. Microelectrodes should also be applied to real world systems as they are developed more efficiently.

REFERENCES

Kondo, T., Udagawa, I., Aikawa, T., Sakamoto, H., Shitanda, I., Hoshi, Y., Itagaki, M., & Yuasa, M. Enhanced Sensitivity for Electrochemical Detection Using Screen-Printed Diamond Electrodes via the Random Microelectrode Effect (2016). *Anal. Chem.* **88**; 3, 1753-1759. DOI: 10.1021/acs.analchem.5b03986